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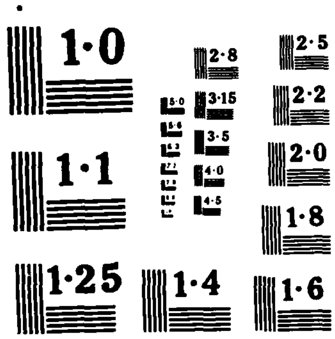
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GAS PHASE INTERACTIONS IN THE SHUTTLE ENVIRONMENT

85-6055

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Abstract

A quadrupole mass spectrometer was flown on STS-4 by the Air Force Geophysics Laboratory. A retarding potential grid located in the ion source distinguished between high and low energy ionic and neutral species in the Shuttle environment. The bulk of the neutral water molecules entering the mass spectrometer appear to be thermal. In contrast, a considerable fraction of water ions, which are formed from charge transfer reactions with ambient O^+, have energies greater than thermal. The high energy species are attributed to non-reactive collisions between the thermal water ions and the high energy incoming flux of ambient neutrals. The energy distributions of the ions are affected more by these interactions because of their greater collision cross sections.

Introduction

A quadrupole mass spectrometer was flown by the Ionospheric Physics Division of AFGL on STS-4 in June and July of 1982. This instrument, designed by the late Dr. Rocco Narcisi and coworkers, measured the ionic and neutral constituents in the vicinity of the Shuttle[1]. A retarding potential analyzer was used to differentiate the fraction of each incoming species with energy greater than a certain cutoff energy from the fraction with less energy. The "non-retarded" (NR) intensity of each species was recorded with -10 V on the retarding grid, whereas the "retarded" (R) intensity was recorded with +2.5 V. Thus, the cutoff energy for neutrals was 2.5 eV. For the ionic species, the cutoff energy depended on vehicle potential, and was in the range 0.5 - 1.5 eV.

The original experimental plan[1] was to interpret the R mode intensity of each species as a measure of the ambient concentration and to attribute the difference between the NR and R mode intensities to the thermal or low energy species formed within the Shuttle environment. In a previous paper[2], we showed that, in the case of the ions, this plan was complicated substantially by reactive and non-reactive scattering processes that occur within the contaminant cloud surrounding the Shuttle. In the present paper, we extend the analysis of the R mode data to the neutral species in the Shuttle environment.

Instrumentation

The Quadrupole Ion/Neutral Mass Spectrometer (QINMS) consists of two packages. The sensor package contains an electron impact ion source, a system of grids, the quadrupole rods and the electron multiplier. The interior of the sensor is sealed with a motor driven cover and is exposed to space during the measurements. The sensor package also contains the rf oscillator, two logarithmic data amplifiers and the high voltage power supply. The second of the two separate packages is the electronics box which contains the command, program, signal conditioning and telemetry circuitry.

On STS-4, the mass spectrometer was mounted in a fixed position approximately three-quarters of the way back in the payload bay. The sensor pointed out over the right wing of the Shuttle (in the +Y direction), and was elevated 12° above horizontal. The sequence of measurements made by the instrument and the number of times the instrument was turned on during the flight have been discussed in a previous paper.[1]

Figure 1 is a schematic diagram of the internal construction of the mass spectrometer. The retarding potential analyzer is labelled the energy analysis grid, and is located between the ion source and the entrance aperture to the quadrupole rods. The "non-retarded" (NR) intensity of each ionic and neutral species was recorded with -10 V on this grid. Because the grid was essentially transparent at this voltage, the NR intensity was a measure of the total flux of each species entering the spectrometer. The "retarded" (R) intensity was recorded with +2.5 V on the grid. This voltage was chosen because the motion of the Orbiter through the atmosphere gives ambient species considerable energy with respect to the Orbiter. In electron volts, this energy is approximately equal to the mass number of the species divided by three. Thus, ambient

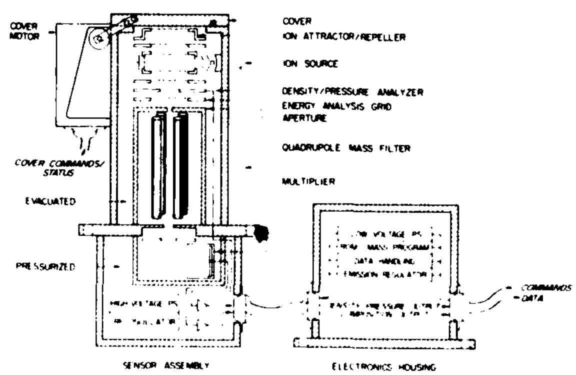

Figure 1: Schematic Diagram of the Quadrupole Ion/ Neutral Mass Spectrometer

species (ions or neutrals ionized in the ion source) easily have enough energy to cross this potential barrier and be detected.

Results and Discussion

The mass spectrometer was not operated continuously on STS-4, but was turned on for many five to fifteen minute periods throughout the flight. The instrument collected one complete mass spectrum approximately every second during these periods. One method which has proved useful in reducing this large volume of data is to first separate out the data taken when the RCS engines were firing and then to calculate an average intensity for each ion and neutral species for each data collection period. This method shows nicely how the overall species concentrations changed during the flight.

The results of using this data reduction technique on neutral water vapor are shown in Figure 2. Averaged NR intensities are plotted as the solid line and the averaged R intensities as the dashed line. Around orbits 5, 18 and 32, there are prominent features in the NR water intensity profile where the water concentration rises about an order of magnitude above the adjacent levels. Narcisi et al.[1] have pointed out the striking correlation between the water concentration and the temperature of the mass spectrometer. The peaks in water concentration are due to the increased surface outgassing rate at higher surface temperature.

An unexpected result is the behavior of the R mode water intensity. Throughout most of the flight, the R intensity was nearly equal to the NR intensity. However, at the same times the total water concentration increased due to the temperature changes, the R mode intensity dropped dramatically to as much as three orders of magnitude below the NR signal. In the water data, this behavior is seen most clearly at orbit 32.

The orbit averages of the neutral NR and R mode mass 17 signals are shown in Figure 3. Because the mass 17 signal is almost entirely due to OH^+ produced from dissociative ionization of water in the ion source, it shows the same behavior as the mass 18 parent water signal. The three large peaks in the NR signal correspond to the water peaks in Figure 2. In addition, the mirror image behavior of the R mode signal is even clearer in the mass 17 data than in the parent water signal.

The final example of the orbit averaged flight histories of neutral NR and R intensities is the mass 16 data shown in Figure 4. Mass 16 ions can be produced in the ion source by ionization of the ambient atomic oxygen and also by dissociative ionization of water. Because of this, the NR and R intensity patterns due to the parent water are somewhat obscured.

We had no influence over the attitude of the Orbiter during the STS-4 flight. Hence, the data in Figures 2-4 were obtained at many different instrument angles of attack (the angle between the centerline of the sensor and the velocity vector). We have evaluated how the intensities of the species in Figures 2-4 varied with angle of attack by sorting the data into 15° angle of attack bins and then calculating bin averages.

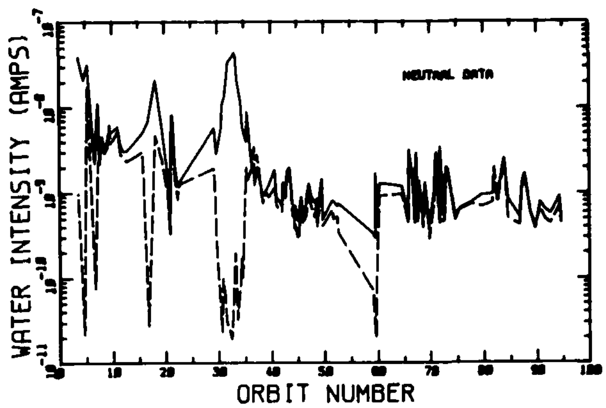

Figure 2: Flight history of neutral water intensity. NR signals are plotted as the solid line. R signals are plotted as the dashed line.

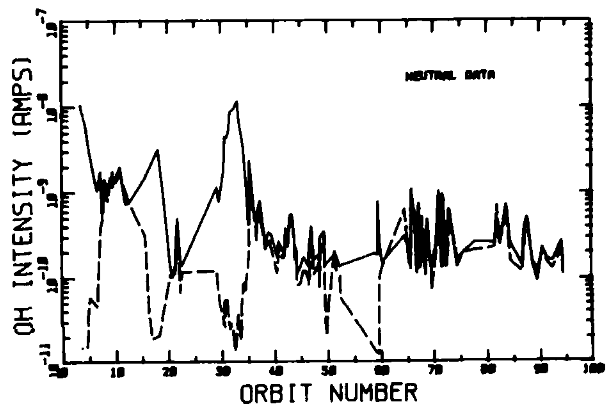

Figure 3: Flight history of neutral mode mass 17 signal.

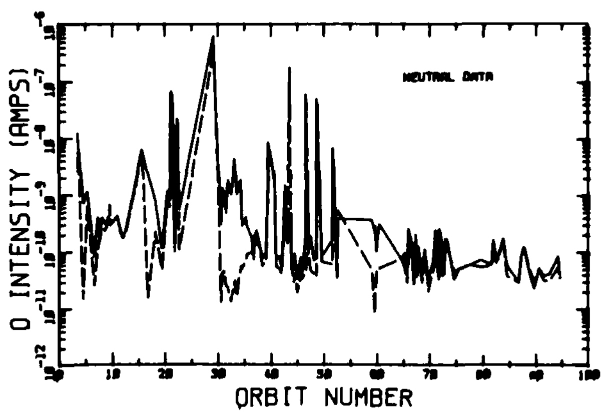

Figure 4: Flight history of neutral mode mass 16 signal.

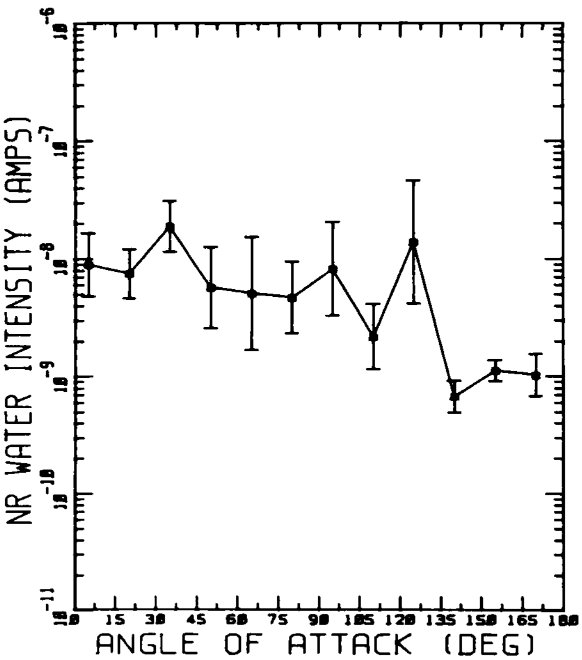

Figure 5: Angle of attack variation of neutral NR water signal.

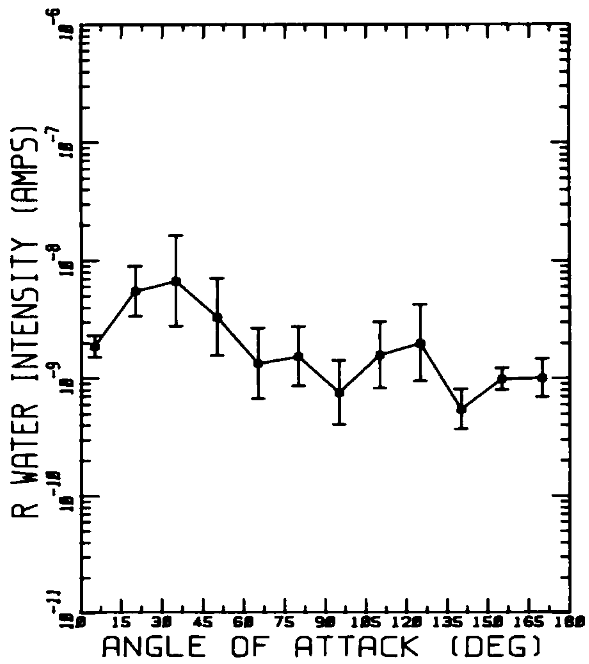

Figure 7: Angle of attack variation of neutral R water signal.

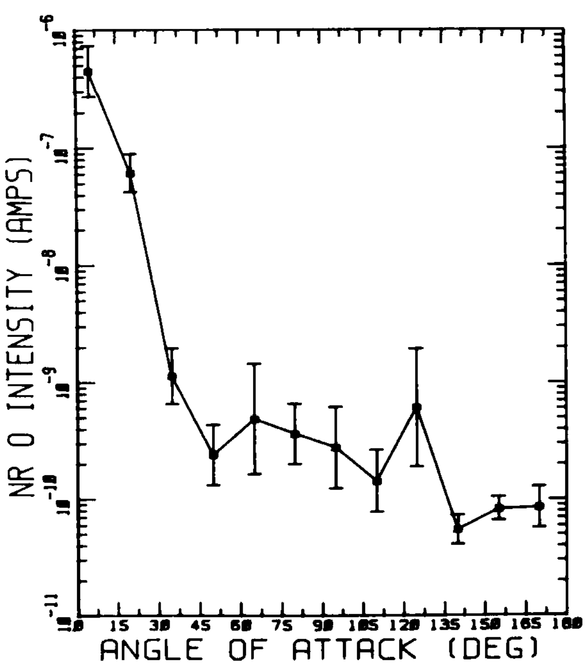

Figure 6: Angle of attack variation of neutral NR atomic oxygen.

Figure 5 shows that there is virtually no variation in NR water intensity with angle of attack. Because there is very little ambient water at Shuttle altitudes, the only source of water in the Shuttle environment is outgassing of the Shuttle surfaces. The water seen by the mass spectrometer may be directed outgassing flux from the surfaces or may come from a cloud that travels with the Shuttle. The flat angle of attack curve is consistent with either explanation.

For comparison, the angle of attack variation in the atomic oxygen signal is plotted in Figure 6. In the first 45°, the intensity of the atomic oxygen falls off by approximately three orders of magnitude and then flattens out into a long tail that extends to 180°. The large signals near ram are due to ambient atomic oxygen and the smaller signals at higher attack angles are due to dissociative ionization of water.

The data in Figure 6 make it clear why the flight history of atomic oxygen in Figure 4 is so different from that of water. The orbits showing the highest intensity of atomic oxygen were taken with the instrument in ram. These large signals are due to ambient atomic oxygen. When the instrument was out of ram, the signal was much lower, and was due to dissociative ionization of water. These lower signals are more characteristic of the water behavior. This is particularly evident at orbit 32 where the mass 16 NR and R signals show the same mirror image shape as the parent water.

Figure 2 shows that the R mode water intensity was nearly equal to the NR intensity throughout most of the flight. This is reflected in Figure 7, where the angle of attack variation of the R mode water signal is plotted. The retarded water signal is as independent of angle of attack as the NR signal. The large differences between the NR and R

signals at orbits 5, 18 and 32 have been averaged out by the sorting procedure.

As mentioned above, we intended to interpret the R mode intensity as a measure of the amount of high kinetic energy species entering the mass spectrometer. The data in Figure 7 seem to indicate that just as much high energy water gets into the instrument when it is pointed into wake as when it is in ram.

It is difficult to explain the apparent detection of high energy water in wake. In a previous paper[2], we discussed a number of mechanisms that could give rise to energetic water ions in the Shuttle environment. The most important of these is collisional scattering between the ambient species and the outgassing water ions that are formed from charge transfer reactions. Similar backscattering could contribute to a flux of high energy neutral water molecules. However, this would be a directed flux moving in the same direction as the ambient species. Because of the position of the mass spectrometer in the payload bay, the body and wings of the Shuttle would prevent this directed flux of molecules from reaching the mass spectrometer in the wake orientation. Even if they are formed in collisions, there is no way that the mass spectrometer could sample these high energy water molecules when it is in wake.

At this time, we must conclude that the apparent high energy neutral water flux detected in wake is likely due to a difference between the effective retarding potential felt by the ions and the potential applied to the retarding grid. However, the mirror image behavior of the NR and R water signals at orbits 5, 18 and 32 indicates that the instrument was not equally affected by this difference at all times during the flight. In particular, it is worth comparing orbits 30-35 to orbits 65-75. In all of these orbits, the Shuttle was in a tail-to-sun orientation with the wings perpendicular to the orbital plane, an attitude that gave an attack angle of $90^{\circ} \pm 20^{\circ}$. Despite this common attitude, the instrument behaved very differently in the two periods. There is a three order of magnitude difference between the NR and R water signals in orbits 30-35, but less than a factor of two difference during orbits 65-75.

At an attack angle of 90°, ambient-contaminant scattering should direct very few high energy water molecules into the mass spectrometer sampling orifice. The large difference between the NR and R signals at orbits 30-35 is consistent with little high energy water, whereas the factor of two difference at orbits 65-75 is not. Hence, we conclude that the retarding potential analyzer was working properly (i.e. gave reasonable results) during orbits 30-35, but was not working properly during orbits 65-75. Similar comparisons of attitude to the rest of the data in Figures 2 and 3 suggest further that the retarding grid worked properly only during the times that the water vapor pressure and the temperature were high.

The apparent anomalous behavior of the retarding potential analyzer may be due to so-called "contact potentials." It is commonly observed in high vacuum ion and electron beam apparatus that the effective potential felt by a charged particle passing through a biased grid may be as much as several volts different from the applied voltage[3,4]. Empirical laboratory experience suggests that the effect is due to adsorbed layers of gas on the grid surfaces. The effective potential of the grid depends strongly on the pressure and composition of the gas in which the grid is immersed.

The effects of adsorbed gases on the electrical properties of metal surfaces have been studied in ultra-high vacuum experiments with single crystal metal surfaces[5]. The adsorbed gas creates an electrical double layer which changes the effective work function of the metal. The change in the work function is equal in magnitude and opposite in sign to the change in the surface potential. The magnitude and even the sign of this effect vary with the type of adsorbed species, the type of metal, the crystal plane of the metal and the degree of surface coverage. Nevertheless, the trend is toward higher work functions with greater surface coverage. This trend generally applies to both adsorbed water and oxygen. As the work function increases, the surface potential becomes more negative, and the effective potential between the metal surface and a reference electrode is reduced.

It is difficult to apply the results of surface potential studies in the controlled environment of an ultra-high vacuum chamber to the relatively uncontrolled environment of the mass spectrometer ion source. The ion source surfaces are made of polycrystaline rather than single crystal metals. Further, the various surfaces may have different temperatures and surface coverages.

The retarding potential analyzer data appear to be valid when both the total water vapor pressure and the mass spectrometer temperature were high. The amount of a surface covered by gas phase molecules is governed by the kinetics of both adsorption and desorption. Despite the increased gas phase water vapor concentration during the periods of valid retarding grid data, the increased temperature may have warmed the grid sufficiently to decrease the surface coverage of water.

The trends described above offer a qualitatively consistent explanation of the neutral mode water data. When the temperature was low, the retarding grid was covered by a large amount of water which caused the effective voltage to be considerably lower than the applied voltage. Low energy water molecules were then able to pass through the retarding grid even during the R mode measurements, leading to the near equality of the NR and R intensities. Conversely, at higher temperatures, the water was driven off the surface of the retarding grid and the effective potential rose closer to the applied potential. The low energy water molecules were stopped by the grid during the R mode measurements, and the difference between the NR and R intensities was large.

If we restrict our attention to orbits 4-8, 15-20 and 30-35, the periods when the retarding potential analyzer appears to have provided valid data, we may draw some qualitative conclusions about the gas phase interactions that occur in the Shuttle environment. During these periods, the R mode water intensity was as much as three orders of magnitude lower than the NR mode intensity; at least 99% of the water molecules entering the mass spectrometer had energy less than the effective potential on the retarding grid.

It is not possible to determine what the actual effective potential on the grid was for these measurements. The applied voltage on the grid for all the R mode measurements was +2.5 V. With this

applied voltage, the effective voltage varied from a value that allowed passage of most of the water molecules to a value that stopped almost all of them. Since the temperature changes that caused the changes in effective voltage were rather small (varying from 5 to 25°C[1]), we expect that rather small changes in the effective voltage caused the very large changes in the NR/R water signal intensity ratio. This suggests that the energy distribution of the water molecules was narrow and that the effective voltage moved from approximately zero to a slightly positive value. The data are consistent with the majority of the neutral water being thermal.

We cannot rule out the possibility that a certain fraction of the neutral water molecules had energy higher than thermal. The energetic component can be detected by the mass spectrometer only when it is in ram. Unfortunately, no neutral ram data was taken during the three periods outlined above.

Throughout the STS-4 flight, the mass spectrometer was commanded to switch between ion and neutral mode data frequently. Accordingly, we have both ion and neutral data from approximately the same times in the flight. The flight histories of orbit averaged ion intensities show that the energy distributions of the ions are substantially different from those of the neutrals. As an example, Figure 8 plots the orbit averages of NR and R mode H_2O^+ intensity for orbits 0 - 40. This portion of the flight contains the periods when the retarding grid was working properly according to the neutral data.

The variations in H_2O^+ signal intensity are due almost entirely to angle of attack changes. Both the ambient O^+ and the contaminant H_2O^+ ions have very strong angle of attack dependences when plotted as in Figure 5-7 despite the fact that the H_2O^+ ions are formed from neutral water molecules by charge transfer reactions.

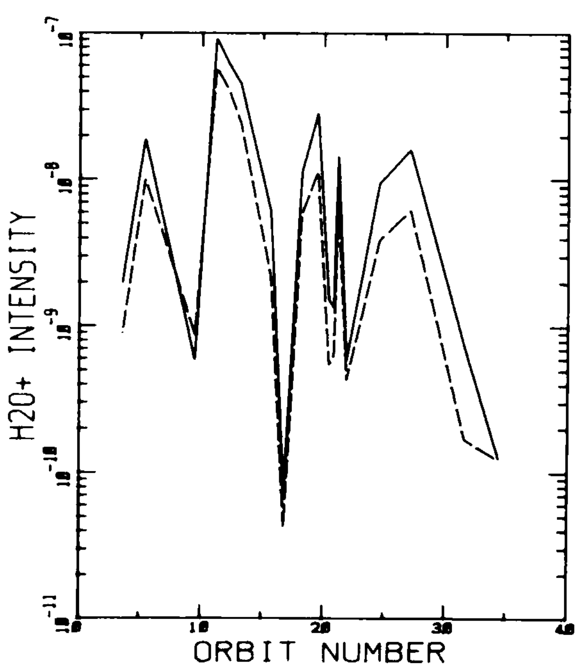

Figure 8: Orbit averaged H_2O^+ NR and R mode ion intensities.

In contrast to the neutral data, the NR and R intensities of the water ions are approximately equal to each other at all times during orbits 0 - 40. In particular, the R intensity is within a factor of two or three of the NR intensity for all points between orbits 16 and 18. During this time, the neutral data showed a two order of magnitude difference between NR and R intensity. We take this as evidence that a larger fraction of the water ions detected by the mass spectrometer may have had energies exceeding the effective potential of the retarding grid.

Ion-dipole and ion-induced dipole forces generally increase ion-neutral collision cross sections by an order of magnitude over the cross sections for comparable neutral-neutral interactions. Because of this, the water ions in the outgassing flow of water from the Shuttle have a much greater chance of colliding with an incoming ambient neutral species. These collisions are a likely source of the high energy species detected by the mass spectrometer.

Conclusions

The retarding potential analyses made by the AFGL quadrupole mass spectrometer aboard STS-4 may have been strongly affected by contact potentials. The effective potential felt by the ions appears to have been as much as several volts less than the applied voltage. The difference between the applied voltage and the effective potential correlates well with the gas phase concentration of water and with the temperature of the instrument.

Variations in the amount of the grid surface covered by water molecules may be the cause of the contact potentials. We propose that the retarding potential grid gave more valid data at higher temperatures. The increased surface temperature may have driven off some of the adsorbed water, leading to lower surface coverage and less difference between the effective grid potential and the applied potential. These observations may be important in the design of future retarding potential analyzers for use in the Shuttle environment.

Despite the variations in the effective retarding grid potential, there were times during the flight when a consistent interpretation of the data was possible. At these times, greater than 99% of the neutral water molecules entering the mass spectrometer had energies less than the effective potential on the grid. This is consistent with the water being thermal. In contrast, the water ions may have had a substantial energetic fraction.

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